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(56) Documents cited

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(58) Field of search

C3R

(54) **Process for the production of aromatic polyesters**

(57) The consistent production of aromatic polyesters is facilitated by the incorporation of a salt, particularly an alkali metal or alkaline earth metal salt, and preferably potassium sulfate, during the reaction procedure. Molded articles made from these polyesters have improved appearance and excellent properties.

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SPECIFICATION

Process for the production of aromatic polyesters

- 5 The present invention relates to an improved process for the production of aromatic polyesters. More particularly, it relates to a process for the production of oxybenzoyl polyesters of aromatic dicarboxylic acids, dihydroxyphenols and p-hydroxybenzoic acid compounds as the starting materials. 5

- It is known that aromatic polyester resins can be produced by various polymerization processes including suspension polymerization and bulk polymerization. Of these, the bulk polymerization process is perhaps the most desirable process in terms of economy. However, since aromatic polyester have a high melting point as compared with aliphatic polyesters, such as polyethylene terephthalate, a higher temperature is required to maintain the aromatic polyesters in a molten state. Consequently, the polymers are often colored and deteriorated in performance. 10 15

Further, difficulty has been experienced in obtaining lot-to-lot consistency in molding characteristics of the resin. Obviously, variations in molding conditions are undesirable in commercial operations and can result in inefficiencies of operation and unacceptable differences in the molded articles.

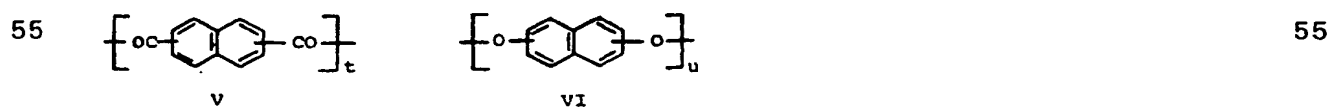
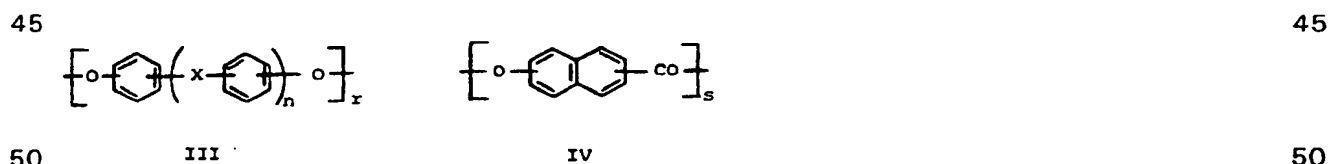
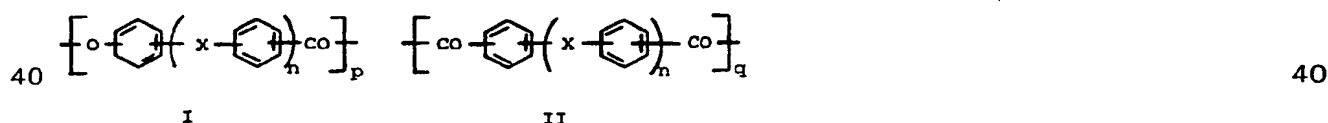
- 20 Much effort has therefore been expended on the development of a process which eliminates the disadvantages discussed above and provide a polyester molding material from which articles of pleasing and uniform appearance and properties can be obtained. 20

- The invention provides a process for preparing an aromatic polyester which comprises the heat condensation of aromatic polyester precursors to form a prepolymer and thereafter 25 advancing the prepolymer to form an aromatic polyester having the required degree of polymerization, wherein a salt is incorporated into the reaction procedure before completion of the polymerization. 25

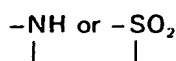
- According to the present invention, there can be consistently produced an aromatic polyester having an extremely low degree of discoloration and an excellent heat stability which has 30 hitherto not been obtainable by the conventional bulk polymerization. 30

The salt, particularly an alkaline earth metal salt or an alkali salt and preferably potassium sulfate, is preferably added to the prepolymer melt prior to advancement of the final product to the desired degree of polymerization.

- The wholly aromatic polyesters towards whose production the present invention is directed 35 preferably contain, as recurrent moieties, at least one structural group selected from groups of the formulae: 35



- 60 where X is a direct bond, -O-, -S-, -CO-, 60



- 65 and n is 0 or 1 and the total of p + q + r + s + t + u in the structural groups present is from 3 65

to 800.

Combinations of the above groups include union of the carbonyl group of Formulae I, II, IV and V with the oxy group of Formulae I, III, IV and VI. In the most general combination groups of all the above formulae can be present in a single copolymer. The simplest embodiment would be homopolymers consisting of groups I or IV. Other combinations include mixtures of groups II and III, II and VI, III and V, V and VI, and I and IV.

The functional groups attached to benzene rings are preferably in the para (1,4) positions, but can also be located in meta (1,3) positions. With respect to the groups containing naphthalene rings, the most desirable locations of the functional groups are 1,4; 1,5 and 2,6, but the functional groups can also be in the meta position to each other.

The symbols p, q, r, s, t and u are 0 or integers and indicate the number of moieties present in the polymer. The total (p + q + r + s + t + u) can vary from 3 to 800 and, when present, the ratio of q/r, q/u, t/r, t/u,

$$\frac{q+t}{r},$$

$$\frac{q+t}{r+u},$$

and

$$\frac{t}{r+u}$$

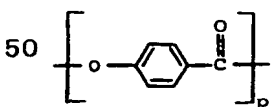
can vary from about 10/11 to about 11/10 with the most preferable ratio being 10/10.

Exemplary of materials from which the groups of Formula I may be obtained are p-hydroxybenzoic acid, phenyl p-hydroxybenzoate, p-acetoxybenzoic acid and isobutyl-p-acetoxybenzoate. Monomers from which groups of Formula II are derivable include terephthalic acid, isophthalic acid, diphenyl terephthalate, diethyl isophthalate, methylethyl terephthalate and the isobutyl half ester of terephthalic acid. Among the compounds from which groups of Formula III result are p,p'-bisphenol; p,p'-oxybisphenol; 4,4'-dihydroxybenzophenone; resorcinol and hydroquinone.

Examples of monomers which yield groups represented by Formula IV are 6-hydroxy-1-naphthoic acid; 5-acetoxy-1-naphthoic acid and phenyl 5-hydroxy-1-naphthoate. Monomers which yield groups represented by Formula V include 1,4-naphthalenedicarboxylic acid; 1,5-naphthalenedicarboxylic acid and 2,6-naphthalenedicarboxylic acid. The diphenyl esters or dicarbonyl chlorides of these acids can also be used. Examples of monomers which yield groups represented by Formula VI are 1,4-dihydroxynaphthalene; 2,6-diacetoxynaphthalene and 1,5-dihydroxynaphthalene.

Particularly preferred for use in the practice of the present invention are monomers which yield oxybenzoyl polyesters.

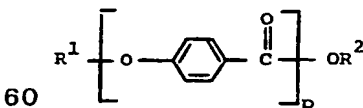
The oxybenzoyl polyesters which may be prepared by the process of the present invention generally contain repeating units of Formula VII:



(VII)

where p is an integer of from 3 to 600.

Preferred oxybenzoyl polyesters are those of Formula VIII:

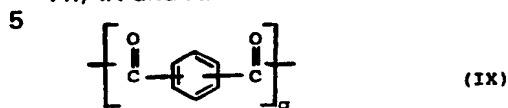


(VIII)

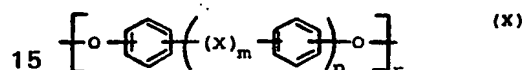
wherein R¹ is selected from benzoyl, lower alkanoyl, or preferably hydrogen; R² is hydrogen, benzyl, lower alkyl, or preferably phenyl; and p is an integer from 3 to 600 and preferably 30 to 200. These values of p correspond to a molecular weight of 1,000 to 72,000 and preferably 3,500 to 25,000. The synthesis of these polyesters is described in detail in U.S. Patent

Application Serial No. 619,577, filed March 1, 1967, and now abandoned, entitled "Polyesters Based on Hydroxybenzoic Acids". This application is referred to in U.S. Patent No. 3,668,300.

Other preferred oxybenzoyl polyesters are copolyesters containing recurring units of Formulae VII, IX and X:



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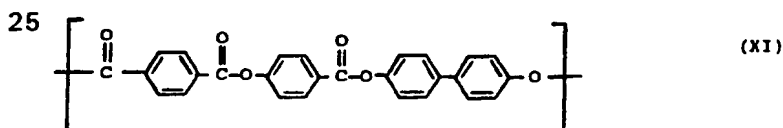


15

wherein X is $-O-$ or $-SO_2-$; m is 0 or 1; n is 0 or 1; $q:r = 10:15$ to $15:10$; $p:q = 1:100$ to $100:1$; $p + q + r = 3$ to 600 and preferably 20 to 200 . The carbonyl groups of the moiety of Formula VII or IX are linked to the oxy groups of a moiety of Formula VIII or X; the oxy groups of the moiety of Formula VII or X are linked to the carbonyl groups of the moiety of Formula VII or IX.

20

The preferred copolyesters are those containing recurring units of Formula XI:



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The synthesis of these polyesters is described in detail in U.S. Patent No. 3,637,595, entitled "P-Oxybenzoyl Copolyesters".

The bulk condensation of aromatic polyesters is described in the patent literature and broadly considered involves an alkanoylation step, for example involving reaction of a dicarboxylic acid, hydroxybenzoic acid and a diol in the presence of an acid anhydride, a prepolymerization step in which the reaction product of the first step is polycondensed to prepare a prepolymer and a polymerization step in which the prepolymer is heated to produce a polycondensate having the desired degree of polymerization.

35

The polyesters useful in the present invention can also be chemically modified by various means such as by inclusion in the polyester of monofunctional reactants such as benzoic acid or tri- or higher functional reactants such as trimesic acid or cyanuric chloride. The benzene rings in these polyesters are preferably unsubstituted but can be substituted with non-interfering substituents, examples of which include halogen such as chlorine or bromine, lower alkoxy such as methoxy and lower alkyl such as methyl.

40

The salt can be an organic or an inorganic salt. However, the use of an alkali metal or alkaline earth metal salt is preferred. More particularly, the following salts can be employed: aluminum acetate, calcium acetate, calcium sulfate, copper acetate, magnesium acetate, magnesium terephthalate, potassium acetate, potassium chloride, potassium phosphate, sodium acetate, sodium sulfate and potassium bisulfate.

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While the salt can be added at any stage of the reaction procedure, it has been found to be particularly effective, and to provide markedly superior properties in the articles molded from the aromatic polyester resin, if the salt is added with the monomer charge.

50

The salt can be added as solid or as a solution at a temperature above the melting point of the salt. It is also possible to add the salt in a solution when incorporation is effected at a lower temperature.

55

Broadly, the salt can be added over a range of from 25.0 parts by weight per million parts by weight of resin (ppm) to 500 ppm.

The exact mechanics by which the processability of the aromatic polyester and the appearance and properties of articles molded from the aromatic polyester is markedly enhanced by the addition of the salt is not fully understood. However, it has been observed that the retention of peak heights in repeated endothermic transitions and the achievement of consistent exothermic transitions is significantly materially improved when the salt is employed in the preparation of the polyesters.

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The aromatic oxybenzoyl polyester polymers are known to display an endothermic transition which corresponds to a melting of polyester. On cooling, an exothermic transition or crystalliza-

65

tion occurs. Where a strong exotherm is observed, the transitions are described as reversible. Observations and the results described in later tables demonstrate that the addition of a salt, such as potassium sulfate, has greatly enhanced the reversibility of the peaks detected in the differential scanning calorimeter (DSC).

5 In determining the retention of peak height, the endotherms for the first and the second heating cycles are recorded on the same scale. The distances from base line to the maxima are determined and the height of the first cycle peak is divided by the height of the second cycle peak ($\times 100$). This value is expressed as "Percent Retention". 5

10 When the endotherms are measured on aromatic oxybenzoyl polyesters which do not contain a salt, it has been found that in the second cycle peaks the onset of transition is difficult to define and the breadth or broadness of the heating curve makes it difficult to determine the peak. Thus, the change in temperature between the onset of transition and the occurrence of the maximum temperature is of a gradual nature, providing a heating curve which resembles a gently sloping or rounded hill. Such a peak is referred to herein as a broad or diffuse peak. 10

15 The second cycle peaks obtained in those instances where a salt has been incorporated during preparation of the aromatic polyesters in accordance with the present invention are sharp and clear with well defined temperature curves and in which the temperatures of the onset of transition and of peak maximum are easily determined. 15

20 The invention will be further illustrated by reference to the following Examples, in which temperatures are in degrees Centigrade. 20

EXAMPLE 1 (Control)

A reaction vessel was charged with 122 kg (268 pounds) of 4,4'-dihydroxy biphenyl, 180 kg (396 pounds) of p-hydroxybenzoic acid, 108 kg (238 pounds) of terephthalic acid, and 313 kg (690 pounds) of acetic anhydride. It was blanketed with nitrogen and heated with stirring to reflux which was continued for a minimum of three hours. Distillation with no return was then initiated and continued for about 5.5 hours while the temperature of the reaction mixture was increased to 315°C. At this point, 0.32 kg (0.71 pounds) of distearyl pentaerythritol diphosphate was added and after 10 minutes the thick melt (93.3% conversion based on distillate yield) was poured into an insulated stainless steel tray and allowed to cool under a nitrogen blanket. It was then removed and ground (size < 1.2 mm, 80% < 0.5 mm). The yield of prepolymer after grinding is 90% by weight. 25 30

The prepolymer was advanced by tumbling under nitrogen in a rotating oven. The prepolymer is heated from ambient temperature to 365°C at a rate of 23°C/hr and cooled immediately. The resulting polymer is obtained as a free flowing powder. 35

EXAMPLE 2

The procedure of Example 1 was repeated exactly using the same materials and procedures with the single exception of the addition of 57 g of potassium sulfate to the reaction vessel with the monomers charge. 40

The DSC (Differential Scanning Calorimeter) endothermic and exothermic peaks for the first and second heating cycles of the polyesters of Examples 1 and 2 were determined and are listed below in Table I.

TABLE 1

| | DSC Endothermic Peak Heating Cycle | | DSC Exotherm Onset Cooling Cycle | | |
|------------------------|---------------------------------------|-------|-------------------------------------|-----|--|
| | 1st | 2nd | 1st | 2nd | |
| Example 1 (Control) | 410 | weak* | 366 | 355 | |
| Example 2 | 421 | 419 | 381 | 381 | |

* The peak recorded here is of a broad and diffuse nature and does not represent a sharp, clear-cut peak. 60

EXAMPLE 3 (Control)

A reaction vessel was charged with 204.0 g (1.095 mole) of 4,4'-dihydroxy biphenyl, 301.1 g (2.18 moles) of p-hydroxybenzoic acid, 181.1 g (1.09 mole) of terephthalic acid, and 526.6 g (5.158 moles) of acetic anhydride, was blanketed with nitrogen and heated with stirring to 65

reflux which was continued for a minimum of three hours. Distillation with no return was then initiated and continued for about 5.5 hours while the temperature of the reaction mixture was increased to 315°C. At this point, 0.76 g of distearyl pentaerythritol diphosphite was added and after 10 minutes the thick melt (93.3% conversion based on distillate yield) was poured into a stainless steel beaker lined with aluminum foil and maintained at 300°C. The prepolymer was kept under a nitrogen blanket at 300°C for 20 hours, then removed, allowed to cool and ground (size < 1.2 mm, 80% < 0.5 mm). The yield of prepolymer after grinding is 90%.

The prepolymer was advanced by tumbling under nitrogen in an aluminum drum which is rotated in an oven. The prepolymer is heated from 204° to 354°C and maintained at the higher temperature for one hour. On cooling, the resulting polymer is obtained as a free flowing powder.

EXAMPLE 4

The procedure of Example 3 was repeated exactly using the same materials and procedures with the single exception of the addition of 0.067 g of potassium sulfate to the reaction vessel with the monomers charge.

The DSC (Differential Scanning Calorimeter) endothermic peaks for the first and second heating cycles of the polyesters of Examples 3 and 4 were determined and are listed below, together with the percent retention of the endothermic peak height, in Table II.

TABLE II

| | Percent Retention of Endo Peak Ht | DSC Endotherm Peak Heating Cycle | |
|------------------------|---|-------------------------------------|------|
| | | 1st | 2nd |
| Example 3 (Control) | 34 | 422 | 417* |
| Example 4 | 107 | 416 | 429 |

* The peak recorded here is of a broad and diffuse nature and does not represent a sharp, clear-cut peak.

Similar comparisons were made for several other polyesters, the control being prepared in accordance with the procedure of Example 1 and the potassium sulfate-containing polyester being prepared in accordance with the procedure of Example 2. The results are listed in Table III below.

TABLE III

| | K ₂ S ₀ 4 Added ppm | Percent Retention of Endo Peak Ht | DSC Endotherm Peak Heating Cycle | |
|-----------|---|---|-------------------------------------|------|
| | | | 1st | 2nd |
| Example 5 | 0 | 27 | 414 | 412* |
| Example 6 | 110 | 71 | 414 | 422 |
| Example 7 | 0 | 40 | 418 | 417* |
| Example 8 | 110 | 75 | 422 | 426 |

* The peak recorded here is of a broad and diffuse nature and does not represent a sharp, clear-cut peak.

As demonstrated, the salt-containing polyester showed a significantly improved percent retention of endothermic peak height.

Comparisons are provided in Table IV between controls prepared in accordance with Example 1 and salt-containing polyesters prepared in accordance with Example 2. The same control was

used in Examples 10, 12, 16, 20 and 22 but is set forth separately in order to provide more immediate comparison with the polyesters of Examples 9, 11, 15, 19 and 21.

TABLE IV

| | <u>Salt</u> | <u>PPM of Cation</u> | <u>Percent Retention</u> | |
|----|-------------|----------------------|--------------------------|----|
| 10 | Ex. 9 | Aluminum Acetate | 98 | 50 |
| | Ex. 10 | Control | 0 | 22 |
| | Ex. 11 | Calcium Acetate | 152 | 35 |
| 15 | Ex. 12 | Control | 0 | 22 |
| | Ex. 13 | Copper Acetate | 84 | 84 |
| | Ex. 14 | Control | 0 | 32 |
| 20 | Ex. 15 | Magnesium Acetate | 126 | 86 |
| | Ex. 16 | Control | 0 | 22 |
| | Ex. 17 | Potassium Chloride | 100 | 70 |
| 25 | Ex. 18 | Control | 0 | 18 |
| | Ex. 19 | Sodium Acetate | 73 | 38 |
| | Ex. 20 | Control | 0 | 22 |
| 30 | Ex. 21 | Sodium Sulfate | 73 | 38 |
| | Ex. 22 | Control | 0 | 22 |

Similar significant improvements in the percent retention as compared to controls having broad or diffuse second cyclic peaks were obtained when the following salts were employed in lieu of those salts specifically recited in Table III; calcium sulphate, magnesium terephthalate, potassium acetate, potassium phosphate and potassium bisulphate.

EXAMPLE 23

A reaction vessel was charged with 156.3 kg (344.5 pounds) of 4,4'-dihydroxy biphenyl, 233 kg (514 pounds) of p-hydroxybenzoic acid, 140 kg (309 pounds) of terephthalic acid, 406 kg (896 pounds) of acetic anhydride, and 57.0 grams of potassium sulfate. It was blanketed with nitrogen and heated with stirring to reflux which was continued for a minimum of three hours. Distillation with no return was then initiated and continued for about 5.5 hours while the temperature of the reaction mixture was increased to 315°C. At this point, 416.0 grams of distearyl pentaerythritol diphosphite was added and after 10 minutes the thick melt (93.3% conversion based on distillation yield) was poured into an insulated stainless steel tray, blanketed with nitrogen and allowed to cool. It was then removed and ground (size < 1.2 mm, 80% < 0.5 mm).

The prepolymer was advanced by tumbling under nitrogen in a rotating oven. The prepolymer is heated from ambient temperature to 365°C and cooled immediately. The resulting polymer is obtained as a free flowing powder. The polymer is characterized by first and second endotherm peaks of 416°C and 418°C and by first and second exotherm points of 377° and 379°.

EXAMPLE 24

A series of 65 runs was made in which polyesters were prepared according to the procedure of Example 23, employing 93 parts per million of potassium sulfate based on the final polymer. The mean average exotherm onset on first cycle was determined to be 377.8° and the mean average exotherm onset for second cycle was determined to be 378.4°. The closeness of these points is extremely significant in relation to consistency and reproducibility in injection molding operations. The products obtained on the injection molding of the polyesters were of high quality.

In the Tables set forth above the amount of salt used is based upon parts per million in the finished polymer.

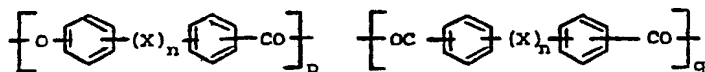
In this specification the term "advancing" is to be understood as indicating polymerization to

the solid state.

CLAIMS

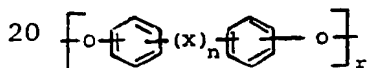
1. A process for preparing an aromatic polyester which comprises the heat condensation of aromatic polyester precursors to form a prepolymer and thereafter advancing the prepolymer to form an aromatic polyester having the required degree of polymerization, wherein a salt is incorporated into the reaction procedure before completion of the polymerization.

2. A process according to claim 1 wherein the polyester contains, as recurrent moieties, at least one structural group selected from groups of the formulae:

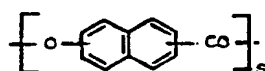


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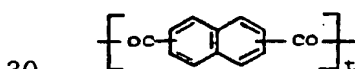
II



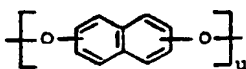
III



IV

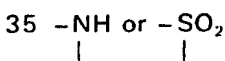


V



VI

where X is -O-, -S-, -CO-,



and n is 0 or 1 and total of p + q + r + s + t + u in the structural groups present is from 3 to 800.

3. A process according to claim 1 or 2 wherein the salt is added in the amount of 25 to 500 parts by weight per million.

4. A process according to claim 1, 2 or 3 wherein the salt is added with the monomer charge.

5. A process according to any one of claims 1 to 4 wherein the salt is an organic salt.

6. A process according to any one of claims 1 to 4 wherein the salt is an inorganic salt.

7. A process according to claim 6 wherein the salt is an alkali metal salt.

8. A process according to claim 7 wherein the salt is potassium sulfate.

9. A process according to claim 6 wherein the salt is an alkaline earth metal salt.

10. A process according to any one of claims 1 to 4 wherein the salt is selected from aluminum acetate, calcium acetate, calcium sulfate, copper acetate, magnesium acetate, magnesium terephthalate, potassium acetate, potassium chloride, potassium phosphate, sodium acetate, sodium sulfate and potassium bisulfate.

11. A process according to claim 1 substantially as described with reference to any one of Examples 2, 4, 6, 8, 9, 11, 13, 15, 17, 19 and 21.

12. Molded articles of an aromatic polyester prepared by a process as claimed in any one of the preceding claims.